1. The classical nucleation theory explains why homogeneous crystal nucleation is difficult: crystals need to exceed a critical size in order to grow, and the ones that are smaller than that will dissolve. In the absence of a seed, a rare, spontaneous fluctuation is needed to form a critical nucleus. The Gibbs free energy of a spherical isotropic nucleus in the liquid is often expressed as

$$\Delta G = -\frac{4}{3}\pi r^3 \overline{\Delta G_{SL}} + 4\pi r^2 \gamma_{SL}$$

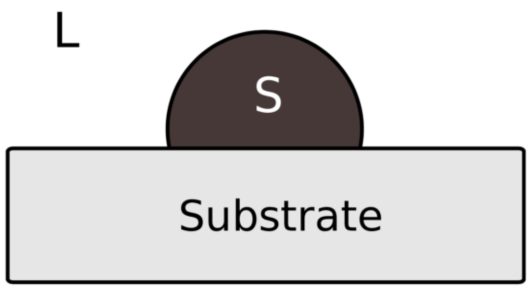
Where $\Delta G_{SL} > 0$ and $\gamma_{SL} > 0$

a) Plot the change of ΔG as a function of r. Determine the size of the critical nucleus γ_c, and the corresponding free energy barrier.

b) What will happen if we add seed crystals to the undercooled liquid phase, given that the seed crystals have the same composition as the nuclei in liquid? Discuss for the cases 1) when the seed crystals are smaller than the critical nucleus, and 2) when they are larger than the critical nucleus.

2. Crystallization can also be facilitated by introducing foreign substances. In fact, heterogeneous nucleation, nucleation starting at a surface, is faster and more common than homogeneous nucleation.

a) Take γ_{SL}, $\gamma_{SS'}$, $\gamma_{S'L}$ to be the interfacial free energy between solid-liquid, solid-substrate, and substrate-liquid, respectively. Can you predict the equilibrium shape of a nucleus formed on the substrate? Assume $\gamma_{SL}+\gamma_{SS'}-\gamma_{S'L}>0$. Hint: you may want to revisit Young's equation introduced in the previous lectures.



b) For simplification, imagine the shape of the solid particle as a truncated sphere. For the nucleus formed on the substrate as in (a), can you write out the expression for the free energy ΔG as a function of its volume?

c) Make a plot to illustrate the relationship between ΔG and the volume of the nucleus both in heterogeneous nucleation and in homogeneous nucleation. How do the free energy barriers of the two compare to each other?

d) Suppose for this system γ_{SL} is constant across all temperatures, and the chemical potential ΔG_{SL} can be expressed as

$$\overline{\Delta G_{SL} S} = H_f \frac{T_m - T}{T_m}$$

Where $H_f > 0$ is the constant of latent heat per unit volume, and T_m is the melting point of the system. Based on these assumptions, can you write down the nucleation free energy barrier as a function of temperature T?

e) According to (d), will the system solidify at $T = T_m$? Write down the condition between γ_{SL}, $\gamma_{SS'}$ and $\gamma_{S'L}$, under which the system will solidify at $T = T_m$?